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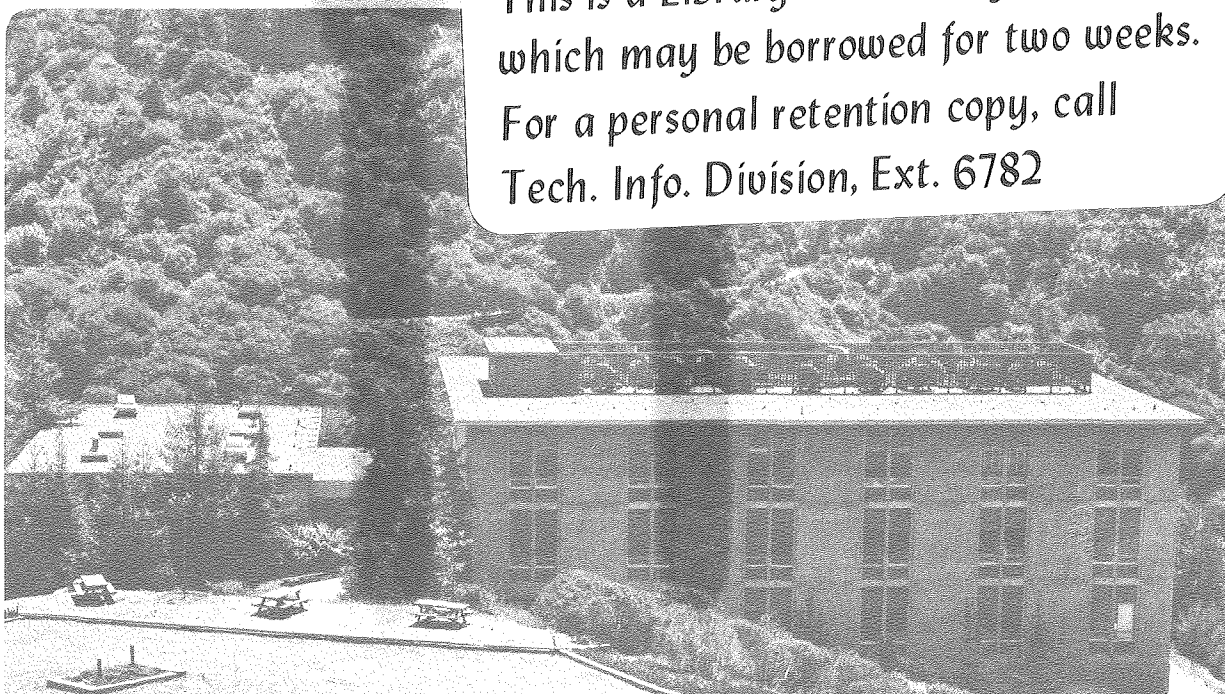
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BENZENE: THE REACTION OF BENZENE WITH ALUMINUM  
TRICHLORIDE REVISITED

Linda S. Benner, Yee-Hing Lai, and  
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On the Purported Fischer-Tropsch Alkylation of Benzene: The  
Reaction of Benzene With Aluminum Trichloride Revisited

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### Abstract

The purported Fischer-Tropsch alkylation of benzene with  $W(CO)_6-AlCl_3$  is shown to be a result of the Lewis acid catalyzed cracking of benzene. Thus,  $^{13}CO$  or  $D_2$  are not incorporated in the alkylbenzene products, nor are they necessary for their formation. The reaction proceeds in the absence of the transition metal "catalyst". A 1:1 mixture of benzene and benzene- $^{13}C$  furnishes the appropriately labeled cracking and condensation products with varying degrees of  $^{13}C$ -scrambling.

In 1979 it was reported<sup>1</sup> that certain transition metal carbonyls  $M_m(CO)_n$  [ $M = W, Rh, Ru, Cr, Co$ ] in the presence of  $AlCl_3$  catalyzed the so-called Fischer-Tropsch alkylation of benzene. The reaction appears of great significance since it is unprecedented and thought to be homogeneous. However, the fact that no labeling control experiments had been carried out, and the assertion that no alkylbenzene formation was observed in the absence of the transition metal, in contrast to the well established Lewis acid chemistry of benzene,<sup>2-9</sup> prompted a reinvestigation of the reported findings.

We have found that alkyl benzenes are formed under the previously reported conditions.<sup>1</sup> However, use of  $D_2$  does not give deuterated products. Similarly, application of  $^{13}C$  does not result in (significant within the error limits of GC/MS) incorporation of the label. Moreover, neither CO or  $H_2$  nor the transition metal are necessary for formation of the observed products. Simply heating benzene and  $AlCl_3$  in a glass pressure vessel furnishes alkyl benzenes in addition to a variety of other products in rather similar proportions to those observed using literature<sup>1</sup> conditions (Table 1). Application of pressure reduces the number of products (resulting in cleaner g.c. traces) and their overall yield.<sup>6</sup> A typical GC trace of the reaction of benzene with  $AlCl_3$  is shown in Figure 1. Surprisingly, such an analysis of the volatile components of the reaction has never been performed.<sup>7</sup>

TABLE 1 Product yields from the reaction of benzene and  $\text{AlCl}_3$  under various reaction conditions.

Conditions:	$[\text{AlCl}_3] = 0.7\text{M}$ $\text{N}_2$ (1 atm), $160^\circ$ , 48h	$[\text{AlCl}_3] = 0.25\text{M}$ $\text{N}_2$ (120 atm), $200^\circ$ , 3h	$[\text{AlCl}_3] = 0.25\text{M}$ , $200^\circ$ , 3h $[\text{W}(\text{CO})_6/\text{diphos}]^b$ , $\text{H}_2$ (100 atm)/CO (20 atm)
% Yield <sup>a</sup> of:			
Toluene	2.187	1.153	1.076, (0.973) <sup>c</sup> , (1.134) <sup>d</sup>
Ethylbenzene	2.680	1.336	1.660, (1.745) <sup>c</sup> , (2.074) <sup>d</sup>
i-Propylbenzene	0.182	0.048	0.174, (0.044) <sup>c</sup> , (0.137) <sup>d</sup>
n-Propylbenzene	0.331	0.090	Trace, (0.069) <sup>c</sup> , (0.012) <sup>d</sup>
Butylbenzenes	0.110	0.011	Trace, (0.021) <sup>c</sup> , (0.044) <sup>d</sup>
Tetralin	0.726	0.019	0.037, (0.035) <sup>c</sup> , (0.050) <sup>d</sup>
Phenylcyclohexane	0.059	0.007	0.019, (0.009) <sup>c</sup> , (0.034) <sup>d</sup>
Biphenyl	1.548	0.081	0.036, (0.129) <sup>c</sup> , (0.159) <sup>d</sup>
Diphenylmethane	0.228	0.021	5.973, (0.151) <sup>c</sup> , (0.562) <sup>d</sup>
Diphenylethane(s)	0.340	0.024	0.146, (0.064) <sup>c</sup> , (0.280) <sup>d</sup>

<sup>a</sup> GC yield calculated using n-octane as internal standard. These products were characterized by GC/MS and co-injection of authentic samples. Approximately 70-80% of benzene was recovered.

<sup>b</sup>  $[\text{W}(\text{CO})_6] = [\text{diphos}] = 0.0047\text{M}$

<sup>c</sup> Yield from reaction in the absence of  $\text{W}(\text{CO})_6$

<sup>d</sup> Yield from reaction in the absence of diphos.

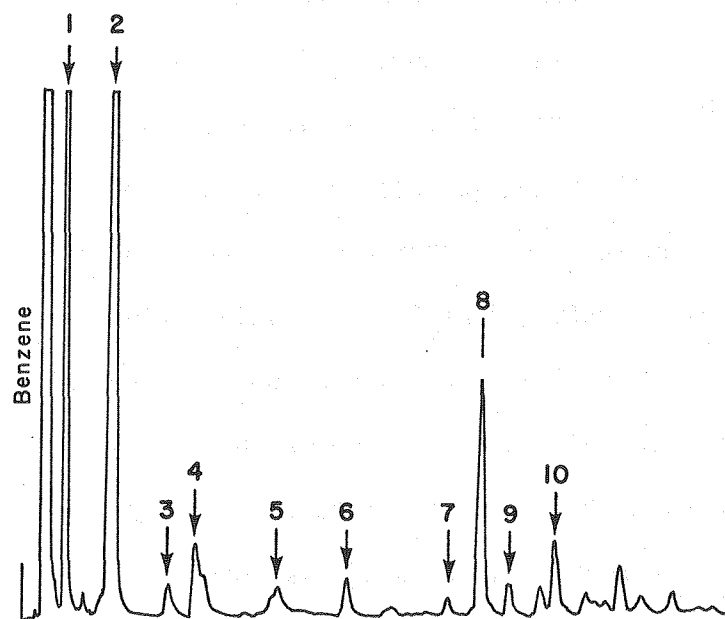


Figure 1. A typical GC trace of the products from the reaction of benzene and  $\text{AlCl}_3$  ( $[\text{AlCl}_3] = 0.7\text{M}$ ,  $\text{N}_2$  (1 atm),  $160^\circ$ , 48h). 1 = toluene, 2 = ethylbenzene, 3 = isopropylbenzene, 4 = *n*-propylbenzene, 5 = butylbenzenes, 6 = tetralin, 7 = phenylcyclohexane, 8 = biphenyl, 9 = diphenylmethane, 10 = 1,2-diphenylethane. 1-10 were identified by GC/MS and coinjection of authentic samples. Other minor products were (GC/MS computer library): methyl-, dimethyl-, and ethyltetralins, phenylcyclopentane, fluorene, methyl- and ethylbiphenyl, 1,1-diphenylethane, phenylnaphthalene, and phenyltetralin. The shoulder in peak 4 could not be resolved.

In the presence of  $W(CO)_6$  (even more so with added diphos) we observe significant amounts of diphenylmethane. Interestingly, the  $W(CO)_6$ -diphos system furnishes much more isopropyl- than *n*-propylbenzene. Since  $AlCl_3$  is a known isomerization catalyst for alkyl groups,<sup>3-10</sup> and its catalytic activity is varied by additives,<sup>11</sup> this result is not surprising. It is also of no consequence to our conclusions. Other Lewis acids such as  $FeCl_3$  and  $AlEt_2(OEt)$  were inactive,  $AlEt_2Cl$  was weakly active.

It had been reported<sup>7</sup> that the major product of the reaction of benzene and  $AlCl_3$  (0.18M) at reflux temperature is phenylcyclohexane and we have confirmed this result. At higher  $AlCl_3$  concentration increasing amounts of alkylbenzenes (mainly toluene and ethylbenzene) are observed suggesting the possibility that phenylcyclohexane as a primary product undergoes cracking reactions to the observed volatile products. However, at higher temperature the reaction is complicated by condensations, secondary cracking, and catalyst deactivation, most likely by  $\pi$ -complexation to higher benzenoids<sup>13</sup> (Figure 2). Such complexation evidently prevents further turnover of benzene and its reaction products. Addition of more  $AlCl_3$  leads to a new spurt in benzene turnover. The hydrogen necessary for alkylbenzene production is envisaged to arise via bi- and polyphenyl formation, as well as Scholl-type condensation reactions.<sup>3,7,9,10,12</sup> Further evidence for the intermediacy of phenylcyclohexane is derived from the observation of very similar product formation to that depicted in Figure 1 on its reaction with  $AlCl_3$ .



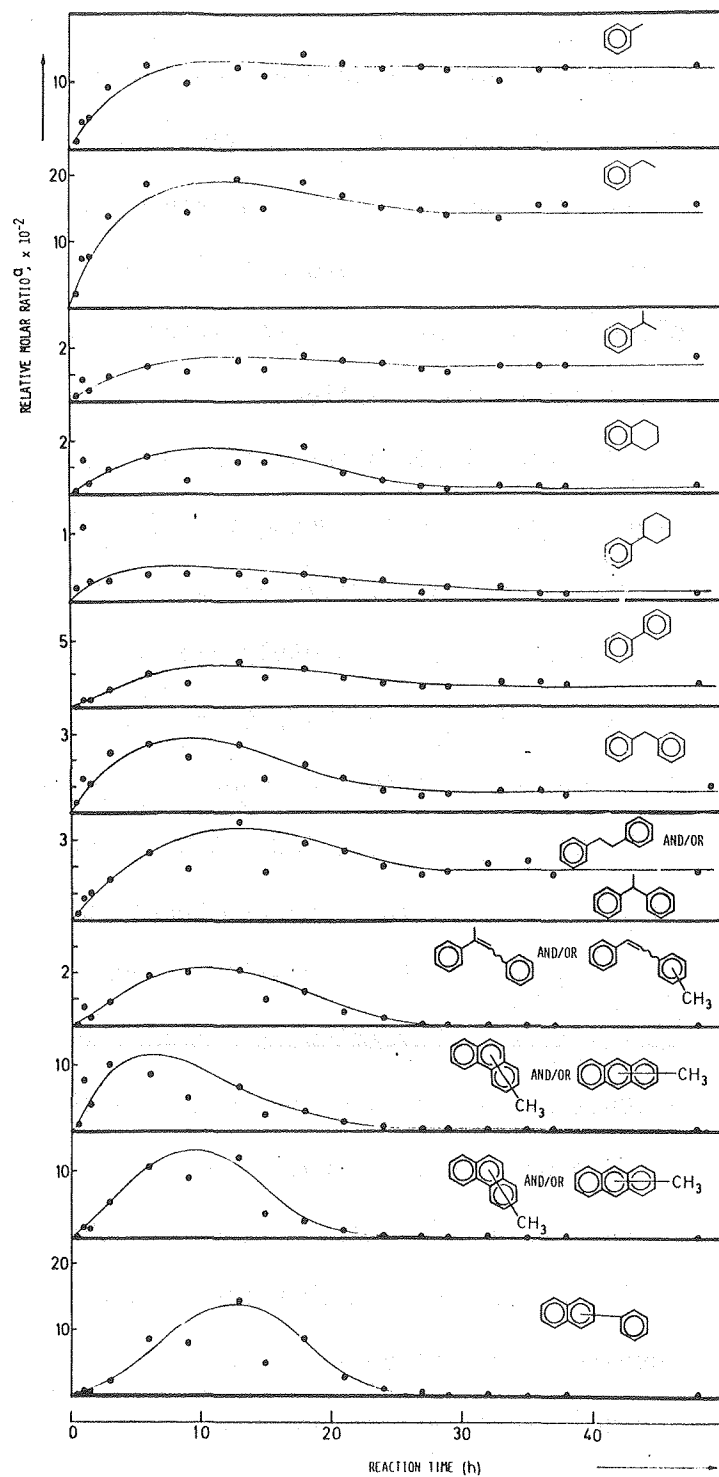


Figure 2. Plot of relative molar ratio of selected products versus reaction time in the  $\text{AlCl}_3$ /benzene reaction ( $[\text{AlCl}_3] = 0.7\text{M}$ ,  $\text{N}_2$  (1 atm),  $160^\circ$ , 48h). n-Octane was used as internal standard. Different scales have been used for clarity. The smooth curves are drawn arbitrarily.

The major alkylbenzene products are toluene and ethylbenzene. This is consistent with the fact that  $\text{AlCl}_3$  catalyzes the cleavage of diphenylalkanes to alkylbenzenes<sup>14</sup> and that the higher members of the latter are fragmented to the above products.<sup>10</sup> The finding that no xylenes and polysubstituted benzenes are detected is most likely due to the low turnover of the reaction. Thus, such products do appear when toluene and other alkylbenzenes react with  $\text{AlCl}_3$ .

In order to shed further light on the mechanism of the benzene cleavage-hydrogenation process several additional labeling experiments were run. Reaction of  $\text{C}_6\text{D}_6$  gave completely labeled products. Not unexpectedly a 1:1 mixture of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  gave complete scrambling. Therefore an equimolar mixture of  $\text{C}_6\text{H}_6$  and  $^{13}\text{C}_6\text{H}_6$  (90% enriched) was exposed to  $\text{AlCl}_3$  [ $\text{N}_2$  (1 atm),  $160^\circ$ , 48h]. Surprisingly,  $^{13}\text{C}$ - $^{12}\text{C}$  exchange (ca. 5%) is observed in recovered "unreacted" benzene and additional scrambling in all other volatile products<sup>15</sup> as analyzed by GC/MS. Despite this perturbation, the mass spectral peak patterns indicate substantially intact incorporation of alkyl chains derived from the original benzene ring. Thus, the connectivity of the initial carbon arrays is extensively preserved in the alkylbenzenes (including annulated and cycloalkylbenzenes) formed. We do not presently understand the mechanism by which label exchange occurs but suspect it to be independent of the alkylation process.

It might perhaps be emphasized that processes such as those described in this communication must play a significant role in any process that attempts to liquefy coal in the presence of Lewis acids.<sup>14,16</sup> In any event it appears that the report on the "Fischer-Tropsch alkylation" of benzene should be approached with caution.

#### Acknowledgments

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- (1) G. Henrici-Olivé and S. Olivé, Angew. Chem., 91, 83 (1979); Angew. Chem., Int. Ed. Engl., 18, 77 (1979).
- (2) C. Friedel and J. M. Crafts, J. Chem. Soc., 115 (1882); Bull. Soc. Chim. Fr., 39, 195, 306 (1883); Compt. rend., 100, 692 (1885).
- (3) C. H. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry", Reinhold Publ. Corp., New York, N.Y., 1941.
- (4) R. Pummerer and J. Binapfl, Chem. Ber., 54, 2768 (1921).
- (5) E. Wertyporoch and H. Sagel, Chem. Ber., 66, 1306 (1933).
- (6) M. G. Gonikberg and A. E. Gavrilova, J. Gen. Chem. USSR, 22, 1429 (1952).
- (7) G. E. Hall and E. A. Johnson, J. Chem. Soc. (C), 2043 (1966). These authors report a detailed analysis of the higher boiling products from the reaction of  $\text{AlCl}_3$  in boiling benzene.
- (8) M. Siskin and J. Porcelli, J. Am. Chem. Soc., 96, 3640 (1974), and the references therein.
- (9) P. Kovacic and A. Kyriakis, J. Am. Chem. Soc., 85, 454 (1963); J. E. Durham and P. Kovacic, J. Polym. Sci., Polym. Lett. Ed., 14, 347 (1976).
- (10) See, R. M. Roberts, E. K. Baylis, and G. J. Fonken, J. Am. Chem. Soc., 85, 3454 (1963); R. M. Roberts, A. A. Khalaf, and R. N. Greene, ibid., 86, 2846 (1964); R. Miethchen, H. Mann, M. Scheel, and I. Stier, Z. Chem., 14, 354 (1974); L. Schmerling and J. A. Vesely, J. Org. Chem., 38, 312 (1973).
- (11) Y. Ono, T. Tanake, and N. Kitajima, J. Catal., 56, 47 (1979); Y. Ono, K. Yamaguchi, and N. Kitajima, ibid., 64, 13 (1980).
- (12) N. P. Buu-Hoi and D. Lavit-Lamy, Bull. Soc. Chim. Fr., 2619 (1966); G. P. Blümer, K. D. Gundermann, and M. Zander, Chem.

- Ber., 109, 1991 (1976); M. Zander, ibid., 92, 2749 (1959); D. Lavit-Lamy and N. P. Buu-Hoi, J. Chem. Soc., Chem. Commun., 92 (1966); N. P. Buu-Hoi, D. Lavit-Lamy, and O. Roussel-Périn, Bull. Soc. Chim. Fr., 1771 (1967).
- (13) H. H. Perkampus and T. Kranz, Z. Phys. Chem., 34, 213 (1962); 38, 295 (1963); H. Sato and Y. Aoyama, Bull. Chem. Soc. Jap., 46, 631 (1973).
- (14) N. D. Taylor and A. T. Bell, Fuel, 50, 499 (1980).
- (15) toluene m/e (% rel intensity): 91(86.6), 92(100 normalized), 93(39.7), 94(12.4), 95(16.1), 96(34), 97(56.8), 98(40), 99(8.7); ethylbenzene: 105(28.0), 106(100), 107(60.7), 108(51.2), 109(10.5), 110(15.1), 111(37.2), 112(50), 113(28.5), 114(13.4); n-propylbenzene: 120(100), 121(56.1), 122(46.6), 123(39.7), 124(4.67), 125(24.0), 126(50.8), 127(31.5), 128(26.5), 129(14.0); n-butylbenzene: 134(100), 135(70.9), 136(56.0), 137(46.3), 138(35.9), 139(26.8), 140(51.1), 141(38.0), 142(28.8), 143(19.2), 144(10.1). Attempts to fit these patterns to calculated intensities based on a statistical analysis of the label distribution expected based on the extent of scrambling observed in the recovered benzene gave variable data always indicating additional but not random scrambling. Similar results were observed for the higher oligophenyls, aromatic systems, and cycloalkylbenzenes.
- (16) J. Falbe, "Chemierohstoffe aus Kohle", Georg Thieme Verlag, Stuttgart, 1977.

